

### 6.4.1 EQUIPMENT AND SUPPLIES

The instrument system that is used to measure pH must be tested before each field trip, and it must be cleaned soon after use. Because of the variety of pH meters and electrodes available, read thoroughly the instruction manual provided by the manufacturer. Every pH instrument must have a log book in which its manufacturer make and model, serial or property number, and all repairs and calibrations are recorded.

pH can be measured either electrometrically or colorimetrically.

- ▶ **The electrometric measurement method uses a hydrogen ion electrode. This is the only technique which is approved for measuring pH values that are to be reported or entered into the USGS data base.**
- ▶ The colorimetric method uses pH “litmus” indicators that change color with a change in pH. The colorimetric method is suitable only when rough estimates of pH are needed; for example, when assessing the volume of acid or base needed to preserve samples; or, when checking that equipment-cleaning solutions have been adequately neutralized prior to disposal.

pH meters are sophisticated electronic instruments that require care in handling and operation. pH instrument systems and buffers must be protected from dirt and extreme heat or freezing conditions while they are in the field and during storage. Keep instrument systems clean and dry when they are not in use. During field travel, protect pH meters and electrodes from being jostled or from sudden impacts.

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer’s instructions.

Table 6.4–1. Equipment and supplies used for measuring pH<sup>1</sup>

[Except for the multiparameter instrument, this equipment is required also for ANC or alkalinity determinations (see NFM 6.6); mL, milliliters; °C, degrees Celsius; mV, millivolt;  $\mu\text{S}/\text{cm}$ , micro-siemens per centimeter at 25 degrees Celsius]

- ✓ pH meter and pH electrodes
  - Battery powered, solid state, with automatic temperature and slope compensation, or multiparameter instrument (possible alternative to separate pH meter and electrode)
  - Range of at least 2 to 12 pH, preferably 0 to 14 pH
  - Accuracy of at least  $\pm 0.1$  units
  - Temperature range of at least 0 to  $+45^{\circ}\text{C}$
  - Millivolt readout with accuracy of  $\pm 1.0$  mV or better for instrument resolution of 0.1 mV
  - Bayonet nut connector (BNC) is recommended
- ✓ pH electrodes, gel-filled or liquid-filled, as appropriate for study objectives and site conditions
- ✓ pH electrode filling solution of appropriate composition and molarity (for liquid-filled electrode)
- ✓ Thermometer, calibrated
- ✓ Buffer solutions, 500 mL each of pH 4, 7, and 10; temperature correction chart(s) for buffers
- ✓ Stand for holding pH electrode (or stand for holding multiparameter instrument system)
- ✓ Bottle, delivery (squeeze), for deionized water
- ✓ Deionized water, maximum conductivity of  $1 \mu\text{S}/\text{cm}$
- ✓ Beakers or measurement vessels, polyethylene or Teflon™ preferable, assorted, 50 to 150 mL, clean but not acid rinsed
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Flowthrough chamber for ground-water measurements (used with meter and electrode equipment)
- ✓ Minnow bucket with tether or equivalent, used for temperature equilibration of buffer solutions
- ✓ Antistatic spray or polish
- ✓ Waste disposal container
- ✓ Stirrer, magnetic with thin insulating pad; or stirrer, mechanical with Teflon™ coated impeller
- ✓ Stirrer bar, magnetic, Teflon™ coated
- ✓ Instrument log book for recording calibrations, maintenance, and repairs

<sup>1</sup>Modify this list to meet the specific needs of the field effort.

**CAUTION:** Before handling pH buffers or other chemicals, refer to Material Safety Data Sheets (MSDS) for safety precautions. Wear eye guards and protective clothing.

### 6.4.1.A pH BUFFER SOLUTIONS

pH measurements are only as accurate as the buffers used for calibration. Use buffers that have been certified traceable to the NIST Standard Reference Material; buffers with a pH of 4, 7, and 10 are available from QWSU.

- ▶ Note that the routine buffers obtained for measurement of pH from 4 to 10 have a high ionic strength. For pH measurements of dilute waters, obtain low ionic-strength buffers.
- ▶ Label buffer and reagent containers with the date when they are received.
- ▶ Label every buffer with its expiration date. Copy this date onto any container into which the buffer is transferred.
- ▶ **Discard buffers on their expiration dates.** The pH of the buffers may have changed substantially because of carbon dioxide absorption, mold growth, or evaporation.

***Take the following precautions to maximize the accuracy of pH measurement (modified from Busenberg and Plummer, 1987):***

1. Always cap buffer bottles to prevent evaporation and contamination from atmospheric carbon dioxide. (In order of greatest to least sensitivity to CO<sub>2</sub> contamination, pH buffer 10 > 7 > 4. Buffers are stable for the short exposure time during electrode calibration.)
2. Never pour used buffer back into stock solution bottles. Never insert an electrode or other material into stock solution bottles containing buffers—always pour the buffer into a separate container.
3. Be very careful not to contaminate the buffer with another buffer or with other fluids (pH 4 buffer is least resistant to contamination).
4. Do not dilute buffer—for example, with water dripping from sensors (more important for pH 7 buffer).
5. Before using buffers, bring them to the temperature of the sample solution, and check with the buffer manufacturer for temperature-correction factors. (In order of greatest to least pH variation with temperature, buffer of pH 10 > 7 > 4.)

## pH ELECTRODES: MAINTENANCE, RECONDITIONING, CLEANING, AND STORAGE 6.4.1.B

The slope and the measured potential of a new electrode should be monitored daily for about 1 week before use (Busenberg and Plummer, 1987). The latest instruments have microprocessors that automatically calculate and display the slope. Some older instruments have a percent-slope readout or (and) millivolt readout. For instruments with a millivolt readout, the measured electrode potential is calculated as the difference between millivolts measured at the known pH of two buffers. Because the theoretical Nernst response is known, slope can be calculated from measured potentials as follows:

$$E = E^0 - S(\text{pH})$$

where

$S$  = slope, and

$E$  = electrode pair potential in mV.

Using two buffers of known pH (1, 2),

$$E_1 = E^0 - S(\text{pH}_1)$$

and

$$E_2 = E^0 - S(\text{pH}_2)$$

or

$$S = \frac{E_2 - E_1}{\text{pH}_1 - \text{pH}_2}$$

and

$$E^0 = E_2 + S(\text{pH}_2).$$

The theoretical slope is temperature dependent; the slope in mV can be calculated as follows:

$$S_t = 0.19841(273.15 + t)$$

where

$t$  = temperature in degrees Celsius, and

$S_t$  = slope at a given temperature.

Normally, electrodes drift from day to day and  $E^0$  typically varies by  $\pm 2$  mV; the slope remains fairly constant to within  $\pm 0.2$  percent Nernst slope after the new electrode has been conditioned. Follow the procedures recommended by the manufacturer. Properly working electrodes commonly drift from about 0.1 to 0.2 mV per hour.

**Electrode maintenance**

Electrodes with gel-filled references require less maintenance than electrodes with liquid-filled references. Follow manufacturer's instructions.

Deterioration of the electrode is normal, and proper maintenance requires that electrode performance be monitored before every water-quality field trip and again at each site. Electrodes can give years of reliable service if maintained by following steps 1–8:

1. Do not handle the glass bulb with fingers. Oily film or scratches on the bulb will interfere with pH measurement. Fingers leave a protein film on the glass that decreases electrode sensitivity.
2. Inspect the electrode and electrode cable for physical damage; for example, check for
  - Scratched or broken bulb.
  - Cut, frayed, or broken cable.
  - Bent or broken connector.
3. **Rinse electrode thoroughly with deionized water before use. Do not wipe electrodes with paper towels or wipes—these scratch the glass bulb. Gently blot** droplets from a wet glass electrode bulb with lens paper or soft tissue by contacting only the droplets to soak up excess solution.

TECHNICAL NOTE: Wiping glass with paper causes a static charge (polarization) that results in drifting, sluggish, and erratic pH readings. It can take many minutes for the electrode to return to normal operation. Clothing also can produce a static charge that affects electrode response.

**Gel-filled electrodes** do not require filling, but should not be left in dilute water for long periods of time. (Salt can leach from the gel into the dilute water and produce a large junction potential, resulting in errors in pH measurement.)

**For liquid-filled electrodes:**

- a. Remove salt crystal deposits from the electrode, membranes, and junctions. Check that the reference junction is not blocked.
  - Rinse off salt buildup with deionized water.
  - Check that you can observe seepage of the filling solution through the junction.
- b. Always unplug the fill hole before making pH measurements, and replug it after use. If using an electrode after it has been in a storage solution, uncap the fill hole and suspend the elec-

trode in air for about 15 minutes. This will allow the filling solution to flush residual storage solution through the porous reference junction and thoroughly wet it.

- c. Check the filling solution level and replenish it if necessary—it should reach the bottom of the fill hole. Filling solutions differ in molarity and composition—always check that you are using the correct filling solution required by the manufacturer for a particular electrode.
  - d. Drain and flush the reference chamber of refillable electrodes, and routinely refill them with the correct filling solution (see manufacturer's recommendations).
4. **Monitor electrode response.** Keep a record of electrode operation in the pH meter log book. Record the Nernst slope reading and the millivolt readings at pH 7 and pH 4 after calibration.
    - Properly working glass electrodes should give approximately 98.0 to 99.5 percent response of that expected from the theoretical Nernst relation (Busenberg and Plummer, 1987). The theoretical Nernst response is 59.16 mV/pH unit at 25°C.
    - A slope of less than 94 percent signals possible electrode deterioration and the need to monitor closely any further decline in slope percent. If possible, replace or recondition the electrode at this point.
    - **Do not use an electrode with a slope of 90 percent or less.**
  5. Keep the electrode bulb moist and capped when not in use. Keep a moist piece of cotton or lint-free tissue in the cap to prevent the bulb from drying out.

### ***Reconditioning liquid-filled electrodes***

Before beginning a field trip, if you are unsure of an electrode's condition or have persistent problems during calibration, use the following procedures to recondition the electrode.

1. Remove the old filling solution from the electrode—
  - a. Place the needle of a 1- or 3-mL syringe into the electrode filling hole (or use other methods of removing the filling solution, such as vacuum extraction or draining).
  - b. Tilt the pH electrode until the filling solution is near the filling hole and the needle tip is covered with the filling solution.
  - c. Pull back on the syringe plunger until the syringe is full.
  - d. Discharge the solution from the syringe into a waste container and repeat steps 1(a) through (d) until all of the filling solution has been removed from the pH electrode chamber.

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2. Flush the pH electrode chamber with deionized water—
  - a. Use a syringe or squeeze bottle to partially fill the pH electrode chamber with deionized water.
  - b. With a syringe, remove the deionized water from the pH electrode chamber.
  - c. As a result of changes in pressure, temperature, and evaporation, crystals may form in the pH electrode chamber. If they form, repeat steps 2(a) and (b) until all crystals have been dissolved and removed from the pH electrode chamber.
3. Fill the electrode chamber with new filling solution—
  - a. Flush the electrode chamber with fresh filling solution using a syringe or a plastic squeeze bottle.
    - Partially fill the pH electrode chamber with filling solution.
    - Tilt the pH electrode so that the filling solution will contact all of the internal electrode surfaces.
    - Remove and discard the filling solution to a waste container.
  - b. Fill the electrode chamber with fresh filling solution until the filling-solution level is just below the fill hole. Be sure to use the correct molarity filling solution.
  - c. Rinse any excess filling solution from the outside of the electrode with deionized water.

Filling solutions might not be interchangeable for different electrodes—  
check manufacturer's instructions.

### ***Electrode cleaning***

Electrodes must be kept clean and the liquid junction free flowing in order to produce accurate pH values. Because of the variety of electrodes available, check the manufacturer's cleaning instructions.

- ▶ Rinse the outside of the electrode thoroughly with deionized water after each use. In general, this should be the only routine cleaning needed.
- ▶ Rejuvenation procedures described by the manufacturer should be used if an electrode becomes clogged or extremely dirty.
  - After completing rejuvenation procedures on a liquid-filled electrode, drain, clean and refill the reference electrode chamber with fresh filling solution. Replace the fill-hole plug, and soak the electrode in storage solution overnight. Retest the electrode. If the procedures fail to remedy the problem, discard the electrode. Document electrode reconditioning or replacement in the instrument log book.
  - Gel-filled electrodes can be rejuvenated in some instances by placing the electrode in warm water (approximately 60°C) for about one minute or less. This procedure rejuvenates the junction by liquifying the salt gel.

***Electrode storage***

Electrodes must be clean before they are stored for any length of time.

**Short-term storage.** Short-term storage methods are appropriate only for in-service electrodes (those used daily or weekly). Storage solutions for short-term storage of electrodes differ with the type of electrode; follow the manufacturer's recommendations. Storage solutions can have a limited shelf life. Unless otherwise instructed by the manufacturer, avoid storing glass hydrogen-ion electrodes in deionized water or concentrated KCl solutions. In the latter case, absorbed potassium reduces the glass sensitivity to hydrogen ions.

- ▶ Store liquid-filled pH electrodes upright.
- ▶ Keep liquid-filled electrodes wet to maximize their accuracy and response time. Store them so that the bulb is fully immersed in proper electrode storage solution between uses at a field site. Before moving to the next field site, replace the plug on the fill hole, fill the protective cap with storage solution, and cover the electrode bulb with the cap.
- ▶ Gel-filled electrodes must only soak in a solution for short periods during measurements. Follow the manufacturer's instructions for storage of gel-filled electrodes.
- ▶ Clean the connector ends and store them in a plastic bag.

**Long-term storage.** pH measuring systems must be stored in an area that is clean, dry, and protected from extremely hot or cold temperatures. For long-term storage of liquid-filled electrodes, drain the filling solution from the electrode, rinse the outside of the electrode with deionized water, and store the electrode dry with a protective cap covering the bulb (put either storage or filling solution in the cap before placing the cap on the bulb if the manufacturer recommends that the bulb be kept moist). Clean the electrode connector ends (with alcohol, if necessary), and store them dry in a sealed plastic bag.